

CARBOXYLATION OF ALCOHOLS WITH CARBON MONOXIDE SUPERSATURATED IN STRONG ACID.
FACILE SYNTHESIS OF 2,2-BIS(4-HALOPHENYL)ACETIC, -PROPIONIC, AND RELATED ACIDSYukio TAKAHASHI,* Norihiko YONEDA,[†] and Hiroshi NAGAI

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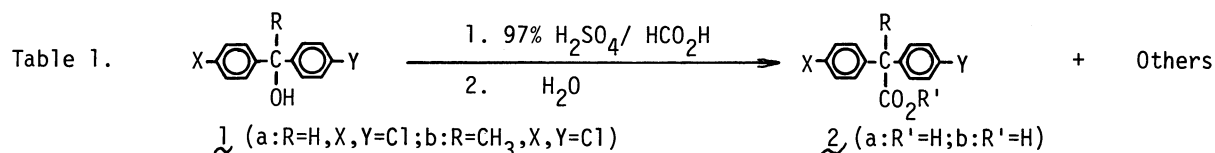
Using 97% H₂SO₄ supersaturated with carbon monoxide, bis(4-halophenyl)methanols, 1,1-bis(4-halophenyl)ethanols and related alcohols were transformed to the carboxylic acids in 60-95% yields.

The Koch-Haaf reaction¹⁾ can not be used for aryl carbinols, because they undergo self-condensation and give complicated products. Particularly, diaryl and triaryl carbinols give highly stable carbenium ions that can hardly react with CO to afford the acyl cations under the ordinary Koch-Haaf reaction conditions.²⁾ A synthetic method for 2,2-bis(4-halophenyl)acetic acids, and -propionic acids, and related acids from the corresponding alcohols in 97% H₂SO₄ supersaturated with CO generated in situ from formic acid is now presented.

Reaction of bis(4-halophenyl)methanols, and -ethanols under a few stirring rate conditions are summarized in Table 1. Under the Koch-Haaf conditions in the literature,¹⁾ bis(4-chlorophenyl)methanol (1a) gave mainly bis(4-chlorophenyl)methyl ether obtained by the hydrolysis of bis(4-chlorophenyl)methyl cation (Expt.No.1). The carboxylated product (2a) was formed in unsatisfactory yield, since the secondary cation can not sufficiently react with CO under the conditions. Under a similar reaction condition without stirring, 2a was obtained in a high yield (Expt.No.2). The increase in the yield of 2a may be produced by the reaction of CO supersaturated in H₂SO₄ with the secondary cation derived from 1a.⁵⁾ The concentration of supersaturated CO was 0.16-0.38 mol/l, achieved by addition of formic acid to 97% H₂SO₄ without stirring.⁶⁾ Under the same condition as in Expt.No.2, however, 1,1-bis(4-chlorophenyl)ethanol (1b) gave the carboxylated product (2b) in a low yield (Expt.No.3). Contrariwise, lengthening of reaction time led to an increase of the yield of 2b (Expt.No.4). The lower reactivity of 1b compared with 1a is produced by the higher stability of the tertiary cation than that of the secondary one.

Without stirring, all the bis(4-halophenyl)methanols except bis(4-iodophenyl)-methanol gave bis(4-halophenyl)acetic acids in good yields. Diphenylmethanol, however, did not give the carboxylated product but afforded unidentified products which might arise from the alkylation of aromatic rings and subsequent sulfonation. This stems from the highly reactive property of diphenylmethyl cation in H₂SO₄ solution.^{7,8)} Strangely enough, bis(4-iodophenyl)methanol could hardly react with supersaturated CO but gave bis(4-iodophenyl)methyl ether. 1,1-Diphenylethanol, giving stable 1,1-diphenylethyl cation in H₂SO₄ solution,⁹⁾ reacted with supersaturated CO and gave 2,2-diphenylpropionic acid in a good yield. Other 1,1-bis-

(4-halophenyl)ethanols reacted with CO and gave the corresponding propionic acids in yields of 60 to 72%. There are yet no facile synthetic methods for tertiary and secondary 2,2-diarylcarboxylic acids.¹⁰⁾ Thus, the present method is a useful one-pot procedure for such carboxylic acids from readily available alcohols.



Expt. No.	Alcohol	Stirring conds.	Time h	Products (yield/%) ^{a,b,c}				
				ArOAr (R'=H) (R'=Ar)	ArOAr	CH ₂ Cl-C(=O)-Cl	others	
1	1a	vigorous ^{d)}	1.3	2 ^{e)}	22	69	-	5 ^{f)}
2	1a	no	1.3	92 ^{e)}	5	0	-	2 ^{f)}
3	1b	no	1.3	16 ^{g)}	-	-	48	26 ^{h)}
4 ⁱ⁾	1b	no	10.2	85 ^{g)}	-	-	1	11 ^{h)}

Alcohol 1 ^{j)}			Stirring conds.	Temp °C	Time h	Yield of 2 ^{b)} %	Mp θ _m /°C
R	X	Y					
H	F	F	no	15 - 16	2.1	95	141.2 - 142.0
H	F	Br	no	15 - 16	2.1	94	131.0 - 132.0
H	Br	Br	no	14 - 16	2.1	76	186.0 - 187.2
H	I	I	no	14 - 16	2.1	14	196.7 - 197.8
CH ₃	H	H	no	14 - 16	10.1	60	173.7 - 174.0
CH ₃	F	F	no	20 - 21	10.1	60	145.0 - 145.2
CH ₃	F	Cl	no	20 - 21	10.1	72	171.0 - 171.8

a) Reaction conditions: 97% H₂SO₄, 22 ml; HCO₂H, 1 ml; alcohols, 2.5 mmol; react.temp, 15 °C. b) Isolated yields based on alcohols employed. c) Ar = Cl-C₆H₄-CH₂-C₆H₄-Cl. d) Stirring speed, ≈1000 rpm. e) Mp, 167 - 168 °C (lit.³⁾, 164 - 166 °C). f) Bis(4-chlorophenyl)methanol. g) Mp, 161 - 162 °C (lit.⁴⁾, 160 - 161 °C). h) For the most part, 4,4'-dichlorobenzophenone. i) React.temp, 20 °C. j) HCO₂H, 6 ml.

References

- 1) For a review: J.Falbe, "New Synthesis with Carbon Monoxide," Springer Verlag, New York (1980), p.372.
- 2) B.S.Friedman, U. S. Patent 3708530(1973);Chem. Abstr., 78, 58064a(1973).
- 3) O.Grimmitt, A.Buck, and R.Egan, Org.Synth., Coll.Vol.III, 270 (1955).
- 4) W.L.Bencze and M.J.Allen, J.Org.Chem., 22, 352(1957).
- 5) M.S.Newman and N.C.Deno, J.Am.Chem.Soc., 73, 3644(1951).
- 6) W.Haaf, Chem.Ber., 99, 1149(1966).
- 7) C.M.Welch and H.A.Smith, J.Am.Chem.Soc., 72, 4748(1950).
- 8) G.A.Olah, J.Am.Chem.Soc., 86, 932(1964).
- 9) V.Gold and F.L.Tye, J.Chem.Soc., 1952, 2172.
- 10) Although some 2,2-diarylacetic acids were prepared from aryl aldehydes and mono substituted benzenes in four steps, the overall yields were poor and 2,2-diarylpropionic acids could not be obtained by this method: Z.Eckstein and D.Rusek, Przem.Chem., 58, 235 (1979);Chem. Abstr., 91, 174970k(1979).

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